## **Teach**

[45] Aug. 29, 1978

[54]	AROMATIC N-SUBSTITUTED
	HALO-SUBSTITUTED-2-PYRROLIDINONES
	AND THEIR UTILITY AS HERBICIDES

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## Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 563,279, Mar. 28, 1975, abandoned.

[56] References Cited

#### U.S. PATENT DOCUMENTS

3,488,732 7/1970 Heiba ...... 260/343.6

OTHER PUBLICATIONS

Adcock et al., J. Amer. Chem. Soc. 96, 1595 (1974).

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[57]

#### **ABSTRACT**

Monocyclic aromatic N-substituted halo-2-pyrrolidinones having the formula

$$Z-CH-C-CH_{2}$$

$$R_{2}$$

$$R_{1}$$

in which X is hydrogen, chlorine or methyl; Y is hydrogen, chlorine or bromine, Z is chlorine or bromine;  $R_2$  is alkyl or hydrogen; R is hydrogen, alkyl, acetyl, chlorine, bromine, fluorine, iodine, trifluoromethyl, nitro, cyano, alkoxy, alkylthio, alkylsulfinyl, alkylsulfonyl, trifluoromethylthio, trifluoromethylsulfinyl, trifluoromethylsulfonyl, pentafluoropropionamido, or 3-methylureido; and  $R_1$  is hydrogen, alkyl, chlorine or trifluoromethyl. The compounds of this invention are prepared by a novel process and are useful as herbicides.

98 Claims, No Drawings

# AROMATIC N-SUBSTITUTED HALO-SUBSTITUTED-2-PYRROLIDINONES AND THEIR UTILITY AS HERBICIDES

This application is a continuation-in-part application of copending application Ser. No. 563,279, now abandoned filed March 28, 1975.

This invention relates to certain novel aromatic N-substituted halo-2-pyrrolidinones (also known as azacy-10 clopentan-3-ones) which are prepared by a novel process and which are useful as herbicides. More specifically, this invention relates to certain monocyclic aromatic or phenyl 2- or N-substituted halo-2-pyrrolidinones, to their preparation and utility of the compounds 15 as herbicides.

The compounds comprising the instant class of compounds correspond to the general formula:

$$Z-CH-C-CH_{2}$$

$$R_{1}$$

$$R_{2}$$

in which X is hydrogen, chlorine or methyl; Y is hydrogen, chlorine or bromine; Z is chlorine or bromine;  $R_2$  is alkyl or hydrogen; R is hydrogen, alkyl, acetyl, chlorine, bromine, fluorine, iodine, trifluoromethyl, nitro, cyano, alkoxy, alkylthio, alkylsulfinyl, alkylsulfonyl, trifluoromethylthio, trifluoromethylsulfinyl, trifluoromethylsulfonyl, pentafluoropropionamido, or 3-methylureido; and  $R_1$  is hydrogen, alkyl, chlorine or trifluoromethyl.

In the above description, the following preferred embodiments are intended for various substituent groups having alkyl, or an alkyl member as in alkoxy, alkylthio, alkylsulfinyl, or alkylsulfonyl, unless otherwise provided for, those members contain from 1 to 4 carbon atoms, inclusive, in both straight chain and branched chain configurations, for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl and the like.

As a consequence of the presence of unsymmetrically substituted carbon centers in certain of the compounds 45 within the scope of this invention, it is recognized that the possibility exists for cis-trans or geometric isomerism. Such cis-trans isomers are stereoisomers whose structures differ only with respect to the arrangement of certain "rigidly" positioned atoms or groups relative to 50 a specified plane of reference. The plane of reference herein is the pyrrolidinone ring. In specifying cis-trans configurations in a monocyclic compound, any of the ring positions having non-identical groups are considered to assign relative configurations. Using the pictoral 55 connotation for representing these relative positions in structural formulas, the pyrrolidinone ring system is considered flat. The atoms or groups under consideration are described as cis when they are on the same side of the plane and trans when they are on opposite sides of 60 the plane (see Gilman's, Organic Chemistry, Vol. I, p. 477).

The compounds of this invention have been found to be active herbicides of a general type. That is, members of the class have been found to be herbicidally effective 65 against a wide range of plant species. A method of controlling undesirable vegetation of the present invention comprises applying an herbicidally effective amount of

the above-described compounds to the area or plant locus where control is desired.

An herbicide is used herein to mean a compound which controls or modifies the growth of plants. By a "growth controlling amount" is meant an amount of compound which causes a modifying effect upon the growth of plants. Such modifying effects include all deviations from natural development, for example, killing, retardation, defoliation, desiccation, regulation, stunting, tillering, stimulation, dwarfing and the like. By "plants", it is meant germinant seeds, emerging seedlings, and established vegetation, including the roots and above-ground portions.

The intermediates for the preparation of the N-mono cyclic aromatic halo-2-pyrrolidinones are the unsaturated N-alkenyl haloacyl anilides obtained by the acylation of the appropriate unsaturated N-alkenyl anilides.

Suitable anilines, that are not commercially available, may be prepared by a number of methods reported in various sources of the chemical literature and various reviews on the subject such as "Synthetic Organic Chemistry" by Wagner and Zook, Chapter 24, John Wiley and Sons, New York, 1961. In the examples to follow, a specific example of the preparation of an intermediate unsaturated N-alkenyl haloacyl anilide is described.

The mono-cyclic aromatic N-substituted halo-2-pyrrolidinones are prepared by several different methods, depending upon the nature of the starting materials and products desired. A preferred method not heretofore disclosed or known in the prior art is the rearrangement reaction of an N-alkenyl containing haloacyl amide in the presence of a catalytic amount of ferrous ion. The use of a solvent is desirable to facilitate processing of the reaction and to aid in the agitation by providing adequate volume, as well as solubilizing the reagents. The preferred solvents include those which are high boiling and which do not interfere with the reaction, for example, diethylene glycol dimethyl ether, dimethyl formamide, dimethyl acetamide, dimethylsulfoxide, mesitylene and the like. Ferrous ion catalyst sources may be provided from various reagents, for example, ferrous chloride, ferrous bromide, iron metal, ferrocene, ferrous acetonyl acetonate and the like.

Since the reaction is a rearrangement of the unsaturated haloacyl amide in the presence of a catalytic amount of ferrous ion, the amounts of reagents is not critical. The reaction is preferably conducted at reflux temperatures. The temperatures for the reaction are best defined between about room temperature and the reflux temperature for the solvent, if one is employed. Preferably, the reaction temperature is between about 50° to about 190° C., more preferably, the temperature range is between about 125° to about 170° C. At the elevated temperatures, the reaction as described hereinabove proceeds rapidly to yield the desired product. In each instance after the reaction is complete, the recovery is carried out by normal work-up procedures, such as crystallization, sublimation, distillation and the like.

Generally, the reaction can be represented by the following equation:

CXY-C

$$R_{2}$$
 $R_{2}$ 
 $R_{2}$ 

wherein X, Y, Z, R, R<sub>1</sub> and R<sub>2</sub> are defined as above.

The compounds of the present invention and intermediates therefor are more particularly illustrated by the following examples which describe their preparation. Following the examples is a table of compounds which 20 are prepared according to the procedures described herein.

#### **EXAMPLE A**

Preparation of Intermediate N-allyl-m-trifluoromethyl 25 aniline from m-trifluoromethyl acetanilide.

N-allyl-m-trifluoromethyl aniline preparation.

m-trifluoromethyl acetanilide was prepared from the aniline by reaction with acetic anhydride. The acetanilide, 192 g., was dissolved in 300 ml. of tetrahydrofuran (THF) and added dropwise with stirring to a slurry of sodium hydride. 24 g., in 200 ml. of THF under a nitrogen atmosphere at ambient temperature. When hydrogen evolution stopped, allylbromide, 121 g. was added and the mixture was allowed to reflux for 1 hour and stir overnight. The mixture was filtered and stripped under vacuum and the residue diluted with methylene chloride, washed with water, dried and stripped under vacuum. Yield was 205 g. of product, N-allyl-m-trifluoromethyl acetanilide.  $n_D^{30}$  1.4532. The product was of sufficient purity to be used in the next step, without further purification.

The product was added to 200 ml. of concentrated hydrochloric acid with 250 ml. of water. The 2-phase system was heated to reflux with stirring until a clear 45 solution resulted in about 2 hours. The mixture was cooled and the product crystallized out. The mixture was treated with 50% sodium hydroxide with cooling to liberate the N-allyl anilide which was extracted with methylene chloride, dried over magnesium sulfate and 50 stripped to give 170 g. of product. Since gas liquid partition chromatography (GLPC) indicated only 85% purity, the material was dissolved in ether and reprecipitated as the hydrochloride with 20% ethereal hydrochloric acid. Yield was 173 g., m.p. 104°-106° C. 55

N-allyl-m-trifluoromethyl-dichloroacetanilide preparation.

Twenty-three and eight tenths grams of N-allyl-m-tri-fluoromethyl aniline hydrochloride was suspended in 200 ml. of methylene chloride, 21 g. of triethylamine 60 was added and the mixture stirred in a water bath at room temperature while 15 g. of dichloroacetyl chloride was added dropwise. After stirring about 30 minutes, after addition was complete, the mixture was washed with dilute ~1% sodium hydroxide, dilute 65 ~1% hydrochloric acid and water, separated and dried over magnesium sulfate and the solvent stripped under vacuum. The product was dissolved in ether and treated

with 10 g. of 20% ethereal hydrochloric acid, the precipitate filtered off and the ether stripped under vacuum to give 25 g. of product,  $n_D^{30}$  1.4740.

#### **EXAMPLE I**

#### Preparation of

N-m-trifluoromethylphenyl-3-chloro-4-chloromethyl-2-pyrrolidinone.

Thirty milliliters of ethylene glycol dimethyl ether (diglyme) was added to 2 g. of ferrous chloride (FeCl<sub>2</sub>.4H<sub>2</sub>O) and heated to the boiling point under a nitrogen blanket and 10 g. of a water-diglyme mixture was removed. To this was added 12.5 g. of N-allyl-m-trifluoromethyl dichloroacetanilide and heating was continued for 15 minutes at reflux and the conversion to product was determined by GLPC. When conversion was complete (about 30 minutes of reflux), the mixture was cooled, diluted with methylene chloride, washed with 5% hydrochloric acid, separated, dried with magnesium sulfate, treated with activated carbon and Florisil, filtered and the solvent removed under vacuum. Yield was 10 g. of oil, n<sub>D</sub><sup>30</sup> 1.5032.

As noted above, stereoisomers are possible in the compounds which possess carbon atoms in the pyrrolidinone ring having non-identical groups attached thereto. The compound of this example is one such compound and is used as an example of the separation, identification and later herbicidal activity of the cis and trans configurations.

The compound from the above procedure, an oil,  $n_D^{30}$  1.5032, was allowed to stand overnight and a portion crystallized. This material was triturated with carbon disulfide and a slurry of crystals was obtained. The crystals were removed by filtering the slurry. This was identified by NMR to be the trans configuration (I). m.p.  $54^{\circ}-55^{\circ}$  C.

Upon chilling the carbon disulfide filtrate, a further crop of crystals was obtained. After separation and drying, these crystals were identified by NMR to have the cis configuration (II), m.p. 79°-80° C.

$$CO-C$$
 $CO-C$ 
 $H$ 
 $CH_2-C$ 
 $CH_2CI$ 
 $CH_2CI$ 

$$CO-C$$
 $CI$ 
 $CH_2-C$ 
 $CH_2CI$ 
 $CH_2CI$ 

#### **EXAMPLE II**

Preparation of N-m-chlorophenyl-3-chloro-4-chloromethyl-2-pyrrolidinone.

Two grams of FeCl<sub>2</sub>.4H<sub>2</sub>O was suspended in 30 ml. of diglyme and heated to reflux under a nitrogen atmosphere while 10 g. of water-diglyme mixture were distilled off. N-allyl m-chloro-dichloroacetanilide, 11.1 g., was added and heating continued for 20 minutes and the extent of reaction determined by GLPC. When conversion was complete (20 minutes), the mixture was cooled, diluted with methylene chloride and washed with 5% hydrochloric acid, separated, dried over magnesium sulfate, treated with Florisil and activated carbon, filtered and the solvent stripped under vacuum. The product, a thick dark oil, crystallized on standing and was purified by recrystallization from carbon tetrachloride. Yield was 2.9 g. of product, m.p. 93°-94° C.

#### **EXAMPLE III**

Preparation of N-phenyl-3,3-dichloro-4-chloromethyl-2-pyrrolidinone.

One gram of FeCl<sub>2</sub>.4H<sub>2</sub>O was suspended in 25 ml. of diglyme and 20 g. of N-allyl-trichloroacetanilide was added and the mixture was heated at reflux under nitrogen. After 15 minutes, conversion to product was complete and the mixture was diluted with benzene and 30 washed with water. The product crystallized from benzene solution and was filtered off. A sample was recrystallized from ethanol, giving an m.p. of 133°-134° C.

#### **EXAMPLE IV**

Preparation of N-m-trifluoromethylphenyl-3-bromo-4-bromomethyl-2-pyrrolidinone.

One gram of anhydrous ferrous bromide (FeBr<sub>2</sub>) was suspended in 15 ml. of diglyme, 9.6 g. of N-allyl-m-tri-fluoromethyl dibromoacetanilide was added and the mixture was heated to reflux under a nitrogen atmosphere for 15 minutes. The mixture was cooled, diluted with methylene chloride, extracted with water and 5% hydrochloric acid solution, dried, treated with florisil, filtered and the solvent stripped under vacuum, Yield was 7.6 g. of a dark liquid.

## EXAMPLE V

Preparation of

N-m-nitrophenyl-3-chloro-4-chloromethyl-2-pyrrolidinone.

A mixture of 10.1 g. of N-allyl-m-nitro-dichloroacetanilide, 15 ml. of diglyme and 1 g. of anhy-55 drous ferrous chloride (FeCl<sub>2</sub>) was heated at reflux under nitrogen for 1 hour and cooled. The mixture was diluted with benzene, washed with 5% hydrochloric acid and the solution treated with magnesium sulfate and activated carbon, filtered through a pad of Florisil 60 7. and the solvent stripped under vacuum. The product, 6 g. of a thick oil, solidified on standing. Trituation with 8. ether gave 3 g. of crystalline solid, m.p. 102°-104° C.

The following is a table of compounds which are prepared according to the aforementioned procedures. 65 Compound numbers have been assigned to them and are used for identification throughout the balance of the specification.

TABLE I

1 H Cl Cl H H H H 133-134 2 Cl Cl Cl H H H H 133-134 3 H Cl Cl H 2-CH <sub>3</sub> 6-CH <sub>3</sub> semi-solid* 5 4 H Cl Cl H 3-Cl H 93-94 6 H Cl Cl H 3-Cl H 100-102 7 CH <sub>3</sub> Cl Cl H H H 1 179-88 8 Cl Cl Cl H H H 1 179-88 8 Cl Cl Cl H 3-Cl 4-Cl 119-121 9 Cl Cl H 3-CF <sub>3</sub> H 100-102 10 CH <sub>3</sub> Cl Cl H 3-CF <sub>3</sub> H 100-102 11 H Cl Cl H 3-CF <sub>3</sub> H 100-104 12 H Cl Cl H 3-CF <sub>3</sub> H 60-63 13 H Br Br H 3-CF <sub>3</sub> H 60-63 13 H Br Br H 3-CF <sub>3</sub> H 102-104 15 H Cl Cl H 3-Cl 5-Cl 80-90 16 H Cl Cl H 3-Cl 5-Cl 80-90 17 H Cl Cl H 3-Cl 5-Cl 80-90 18 H Cl Cl H 3-Cl 5-Cl 80-90 19 Cl Cl Cl CH 3-CF <sub>3</sub> H 1.5020 20 Cl Cl Cl CH 3-CF <sub>3</sub> H 1.5526 21 Cl Cl Cl H 3-CF <sub>3</sub> H 1.5526 22 H Cl Cl H 3-CF <sub>3</sub> H 1.5526 23 Cl Cl Cl Cl H 3-CF <sub>3</sub> H 1.5526 24 H Cl Cl H 3-CF <sub>3</sub> H 1.5526 25 H Cl Cl Cl H 3-CF <sub>3</sub> H 1.5328 26 H Cl Cl H 3-CF <sub>3</sub> H 1.5328 27 H Cl Cl H 3-CF <sub>3</sub> H 1.5328 28 H Cl Cl H 3-CF <sub>3</sub> H 1.5328 29 H Cl Cl H 3-CF <sub>3</sub> H 1.5328 29 H Cl Cl H 3-CF <sub>3</sub> H 1.5328 30 H Cl Cl H 3-CF <sub>3</sub> H 1.5328 31 H Cl Cl H 3-CF <sub>3</sub> H 1.5328 32 H Cl Cl H 3-CF <sub>3</sub> H 1.5328 33 H Cl Cl H 3-CF <sub>3</sub> H 1.5328 34 H Cl Cl H 3-CF <sub>3</sub> H 1.5328 35 H Cl Cl H 3-CF <sub>3</sub> H 1.5328 36 H Cl Cl H 3-CF <sub>3</sub> H 1.5328 37 H Cl Cl H 3-CF <sub>3</sub> H 1.5530 37 H Cl Cl H 3-CF <sub>3</sub> H 1.5530 38 H Cl Cl H 3-CF <sub>3</sub> H 1.5530 39 H Cl Cl H 3-CF <sub>3</sub> H 1.5530 37 H Cl Cl H 3-CF <sub>3</sub> H 1.5530 38 H Cl Cl H 3-CF <sub>3</sub> H 1.5530 39 H Cl Cl H 3-CF <sub>3</sub> H 1.5530 37 H Cl Cl H 3-CF <sub>3</sub> H 1.5530 38 H Cl Cl H 3-CF <sub>3</sub> H 1.5530 39 H Cl Cl H 3-CF <sub>3</sub> H 1.5530 30 H Cl Cl H 3-CF <sub>3</sub> H 1.5974 40 H Cl Cl H 3-CF <sub>3</sub> H 1.5934 41 H Cl Cl H 3-CF <sub>3</sub> H 1.5934 41 H Cl Cl H 3-CF <sub>3</sub> H 1.4993 35 H Cl Cl H 3-CF <sub>3</sub> H 1.4993 35 H Cl Cl H 3-CF <sub>3</sub> H 1.4993 36 H Cl Cl H 3-CF <sub>3</sub> H 1.4993 37 H Cl Cl H 3-CF <sub>3</sub> H 1.4910 38 H Cl Cl H 3-CF <sub>3</sub> H 1.4910 39 H Cl Cl H 3-CF <sub>3</sub> H 1.4910 40 H Cl Cl H 3-CF <sub>3</sub> H 1.4910 41 H Cl Cl H 3-CF <sub>3</sub> H 1.4910	0	Compound No.	<b>X</b>	Y	Z	$R_2$	R	R <sub>i</sub>	m.p. $^{\circ}_{D}$ C. or $n_{D}^{30}$
5		2	Cl	Cl	Cl Cl	H H	H	H H	85-90 133-134 semi-
8 C1 C1 C1 H 3-CI 4-CI 119-121 9 C1 C1 C1 H 3-CF <sub>3</sub> H 100-102 10 CH <sub>3</sub> C1 C1 H 3-CF <sub>3</sub> H 76-78 0 11 H C1 C1 H 4-CH <sub>3</sub> H 100-104 112 H C1 C1 H 3-F H 60-63 113 H Br Br H 3-CF <sub>3</sub> H 129-121 115 H C1 C1 H 3-CI 5-CI 80-90 116 H C1 C1 H 3-CI 5-CI 80-90 116 H C1 C1 H 3-CN H 1.5020 117 H C1 C1 C1 H 3-CN H 1.5550 118 H C1 C1 H 3-CN H 1.5550 120 C1 C1 C1 C1 H 3-CN H 1.5550 120 C1 C1 C1 C1 H 3-CN H 1.5122 121 C1 C1 C1 C1 H 3-CN H 1.5122 122 H C1 C1 C1 H 3-CF <sub>3</sub> H 1.5122 123 C1 C1 C1 C1 H 3-CF <sub>3</sub> H 1.5328 10 24 H C1 C1 H 3-CF <sub>3</sub> H 1.5328 10 25 H C1 C1 H 3-CF <sub>3</sub> H 1.5328 10 26 H C1 C1 H 3-CF <sub>3</sub> H 1.5328 11 H C1 C1 H 3-CF <sub>3</sub> C H 1.5263 12 H C1 C1 H 3-CF <sub>3</sub> C H 1.5263 13 H C1 C1 H 3-CF <sub>3</sub> C H 1.5763 14 H C1 C1 H 3-CF <sub>3</sub> C H 1.5763 15 H C1 C1 H 3-CF <sub>3</sub> C H 1.5228 16 H C1 C1 H 3-CF <sub>3</sub> C H 1.5228 17 H C1 C1 H 3-CF <sub>3</sub> C H 1.5228 18 H C1 C1 H 3-CF <sub>3</sub> C H 1.5228 19 H C1 C1 H 3-CF <sub>3</sub> C H 1.5228 29 H C1 C1 H 3-CF <sub>3</sub> C H 1.5228 30 H C1 C1 H 3-CF <sub>3</sub> C H 1.5228 30 H C1 C1 H 3-CF <sub>3</sub> C H 1.5228 31 H C1 C1 H 3-CF <sub>3</sub> C H 1.5228 32 H C1 C1 H 3-CF <sub>3</sub> C H 1.5228 33 H C1 C1 H 3-CF <sub>3</sub> C H 1.5228 34 H C1 C1 H 3-CF <sub>3</sub> C H 1.5228 35 H C1 C1 H 3-CF <sub>3</sub> C H 1.5228 36 H C1 C1 H 3-CF <sub>3</sub> C H 1.5228 37 H C1 C1 H 3-CF <sub>3</sub> C H 1.5228 38 H C1 C1 H 3-CF <sub>3</sub> C H 1.5228 39 H C1 C1 H 3-CF <sub>3</sub> C H 1.5228 30 H C1 C1 H 3-CF <sub>3</sub> C H 1.5228 31 H C1 C1 H 3-CF <sub>3</sub> C H 1.5228 32 H C1 C1 H 3-CF <sub>3</sub> C H 1.4993 33 H C1 C1 H 3-CF <sub>3</sub> C H 1.4993 35 H C1 C1 H 3-CF <sub>3</sub> C H 1.4993 36 H C1 C1 H 3-CF <sub>3</sub> C H 1.4910 47 H C1 C1 H 3-CF <sub>3</sub> C H 1.4910 48 H C1 C1 H 3-CF <sub>3</sub> C H 1.4910 49 H C1 C1 H 3-CF <sub>3</sub> C H 1.4910 40 H C1 C1 H 3-CF <sub>3</sub> C H 1.4910 41 H C1 C1 H 3-CF <sub>3</sub> C H 1.4910 42 (cis) H C1 C1 H 3-CF <sub>3</sub> C H 1.4910	5	5 6	H H	Cl Cl	Cl Cl	H H	4-Cl 3-CF <sub>3</sub>	H H	93-94 100-102 1.5032
14 H Cl Cl H 3-Cl Cl H 19-121 15 H Cl Cl H 3-NO <sub>2</sub> H 102-104 16 H Cl Cl H 3-Cl 5-Cl 80-90 5 17 H Cl Cl CH 3-CF <sub>3</sub> H 1.5020 19 Cl Cl Cl H 3-CN H 1.5550 19 Cl Cl Cl CH 3-CF <sub>3</sub> H 1.5122 20 Cl Cl Cl Cl H 3-CN H 1.5122 21 Cl Cl Cl H 3-CN H 1.5122 22 H Cl Cl H 3-CN H 1.5263 0 23 Cl Cl Cl Cl H 3-CF <sub>3</sub> 4-Cl 1.5263 0 24 H Cl Cl H 3-CF <sub>3</sub> 4-Cl 109-112 25 H Cl Cl H 3-CF <sub>3</sub> S H 1.5328 25 H Cl Cl H 3-CF <sub>3</sub> S H 1.5328 25 H Cl Cl H 3-CF <sub>3</sub> S H 1.5974 26 H Cl Cl H 3-CF <sub>3</sub> S H 1.5763 28 H Cl Cl H 3-CF <sub>3</sub> SO H 1.5763 28 H Cl Cl H 3-CF <sub>3</sub> SO H 1.5763 28 H Cl Cl H 3-CF <sub>3</sub> SO H 1.5763 28 H Cl Cl H 3-CF <sub>3</sub> SO H 1.5763 29 H Cl Cl H 3-CF <sub>3</sub> SO H 1.5248 29 H Cl Cl H 3-CF <sub>3</sub> SO H 1.5228 30 H Cl Cl H 3-CF <sub>3</sub> SO H 1.5228 30 H Cl Cl H 3-CF <sub>3</sub> SO H 1.5228 31 H Cl Cl H 3-CF <sub>3</sub> SO H 1.5228 32 H Cl Cl H 3-CF <sub>3</sub> SO H 1.5228 33 H Cl Cl H 3-CF <sub>3</sub> SO H 1.5238 34 H Cl Cl H 3-CF <sub>3</sub> SO H 1.5228 35 H Cl Cl H 3-CF <sub>3</sub> SO H 1.5238 36 H Cl Cl H 3-CF <sub>3</sub> O H 17-121 37 H Cl Cl H 3-CF <sub>3</sub> O H 17-121 38 H Cl Cl H 3-CF <sub>3</sub> H 1.4993 39 H Cl Cl H 3-CF <sub>3</sub> H 1.4993 30 H Cl Cl H 3-CF <sub>3</sub> H 1.4993 31 H Cl Cl H 3-CF <sub>3</sub> H 1.4990 32 H Cl Cl H 3-CF <sub>3</sub> H 1.4910 33 H Cl Cl H 3-CF <sub>3</sub> H 1.4910 44 H Cl Cl H 3-CF <sub>3</sub> CONH H 130-132 45 H Cl Cl H 3-CF <sub>3</sub> CONH H 170-172 46 Cis) H Cl Cl H 3-CF <sub>3</sub> H 1.4910 47 H Cl Cl H 3-CF <sub>3</sub> H 1.4910 48 H Cl Cl H 3-CF <sub>3</sub> H 1.4910 40 H Cl Cl H 3-CF <sub>3</sub> H 1.4910 41 H Cl Cl H 3-CF <sub>3</sub> H 1.4910 42 (cis) H Cl Cl H 3-CF <sub>3</sub> H 79-80	0	9 10 11 12	Cl Cl CH <sub>3</sub> H H	Cl Cl Cl	Cl Cl Cl	H H H H	3-CF <sub>3</sub> 3-CF <sub>3</sub> 4-CH <sub>3</sub> 3-F	H H H H	100-102 76-78 100-104 60-63 dark
22 H Cl Cl H 3-CF <sub>3</sub> 4-Cl 1.5263 23 Cl Cl Cl H 3-CF <sub>3</sub> 4-Cl 109-112 24 H Cl Cl H 3-CF <sub>3</sub> S H 1.5328 25 H Cl Cl H 3-CH <sub>3</sub> S H 1.5974 26 H Cl Cl H 3-CH <sub>3</sub> S H 1.5974 26 H Cl Cl H 3-CF <sub>3</sub> SO H 1.5248 27 H Cl Cl H 3-CH <sub>3</sub> SO H 1.5248 28 H Cl Cl H 3-CH <sub>3</sub> SO <sub>2</sub> H glass* 29 H Cl Cl H 3-CF <sub>3</sub> SO <sub>2</sub> H 1.5228 30 H Cl Cl H 3-CF <sub>3</sub> SO <sub>2</sub> H 1.5228 30 H Cl Cl H 3-CF <sub>3</sub> 5-CF <sub>3</sub> 1.4690 5 31 H Cl Cl H 3-CH <sub>3</sub> O H 95-99 32 H Cl Cl H 3-CH <sub>3</sub> O H 95-99 32 H Cl Cl H 3-CH <sub>3</sub> CO H 117-121 33 H Cl Cl H 3-CH <sub>3</sub> H 89-91 34 H H Cl H 3-CF <sub>3</sub> H 1.4993 35 H Cl Cl H 3-Br H 103-105 36 H Cl Cl H 3-Br H 103-105 36 H Cl Cl H 3-Br H 107-109 0 38 H Cl Cl H 3-I H 107-109 0 38 H Cl Cl H 3-CF <sub>3</sub> H 1.4910 40 H Cl Cl H 3-CF <sub>3</sub> H 1.4910 40 H Cl Cl H 3-CF <sub>3</sub> H 1.4910 41 H Cl Cl H 3-CF <sub>3</sub> H 1.4910 42 (cis) H Cl Cl H 3-CF <sub>3</sub> H 79-80 43 5 (trans) H Cl Cl H 3-CF <sub>3</sub> H 79-80	5	15 16 17 18 19 20	H H H Cl Cl	Cl Cl Cl Cl	Cl Cl Cl Cl Cl	H CH <sub>3</sub> H H CH <sub>3</sub>	3-NO <sub>2</sub> 3-Cl 3-CF <sub>3</sub> 3-CN 3-Cl 3-CF <sub>3</sub>	H 5-Cl H H 5-Cl H	119-121 102-104 80-90 1.5020 1.5550 1.5795 1.5122 dark red
30 H Cl Cl H 3-CF <sub>3</sub> SO <sub>2</sub> H 1.5228 30 H Cl Cl H 3-CF <sub>3</sub> 5-CF <sub>3</sub> 1.4690 5 31 H Cl Cl H 3-CH <sub>3</sub> O H 95-99 32 H Cl Cl H 3-CH <sub>3</sub> CO H 117-121 33 H Cl Cl H 3-CH <sub>3</sub> H 89-91 34 H H Cl H 3-CF <sub>3</sub> H 1.4993 35 H Cl Cl H 3-Br H 103-105 36 H Cl Cl H 2-Cl H 1.5530 37 H Cl Cl H 3-I H 107-109 0 38 H Cl Cl H 4-CH <sub>3</sub> O H 123-125 39 H Cl Cl H 4-CH <sub>3</sub> O H 123-125 39 H Cl Cl H 2-CF <sub>3</sub> H 1.4910 40 H Cl Cl H 3-CF <sub>3</sub> H 1.4910 40 H Cl Cl H 3-CF <sub>3</sub> H 1.79-80 41 H Cl Cl H 3-CF <sub>3</sub> H 79-80 43 5 (trans) H Cl Cl H 3-CF <sub>3</sub> H 54-55	0	23 24 25 26 27 28	Cl H H H H	CI CI CI CI CI	CI CI CI CI CI	H H H H	3-CH <sub>3</sub> S 3-CF <sub>3</sub> SO 3-CH <sub>3</sub> SO 3-CH <sub>3</sub> SO <sub>2</sub>	4-Cl H H H H	1.5263 109-112 1.5328 1.5974 1.5248 1.5763 glass*
0 38 H Cl Cl H 4-CH <sub>3</sub> O H 123-125 39 H Cl Cl H 2-CF <sub>3</sub> H 1.4910 40 H Cl Cl H 3-C <sub>2</sub> F <sub>5</sub> CONH H 130-132 41 H Cl Cl H 3-CH <sub>3</sub> NHCONH H 170-172 42 (cis) H Cl Cl H 3-CF <sub>3</sub> H 79-80 43 5 (trans) H Cl Cl H 3-CF <sub>3</sub> H 54-55	5	30 31 32	H H H H	Cl Cl Cl H	CI	H H H H	3-CF <sub>3</sub> SO <sub>2</sub> 3-CF <sub>3</sub> 3-CH <sub>3</sub> O 3-CH <sub>3</sub> CO 3-CH <sub>3</sub>	5-CF <sub>3</sub> H H H H	1.4690 95-99 117-121 89-91 1.4993
(cis) H Cl Cl H 3-CF <sub>3</sub> H 79-80 43 5 (trans) H Cl Cl H 3-CF <sub>3</sub> H 54-55	0	38 39 40 41	H H H H	Cl Cl Cl Cl	CI CI CI CI CI	H H H H	2-Cl 3-I 4-CH <sub>3</sub> O 2-CF <sub>3</sub>	H H H	1.5530 107-109 123-125 1.4910 130-132
		(cis) 43							
	5		<del></del>					H	54-55

\*=Structure confirmed by infrared analysis.

The foregoing compounds may be designated:

- 1. 1-phenyl-3-chloro-4-chloromethyl-2-pyrrolidinone
- 50 2. 1-phenyl-3,3-dichloro-4-chloromethyl-2-pyrrolidinone
  - 3. 1-(2',6'-dimethylphenyl)-3-chloro-4-chloromethyl-2-pyrrolidinone
  - 4. 1-m-chlorophenyl-3-chloro-4-chloromethyl-2-pyr-rolidinone
  - 5. 1-p-chlorophenyl-3-chloro-4-chloromethyl-2-pyr-rolidinone
  - 6. 1-m-trifluoromethylphenyl-3-chloro-4-chloromethyl-2-pyrrolidinone
  - 7. 1-phenyl-3-chloro-3-methyl-4-chloromethyl-2-pyr-rolidinone
  - 8. 1(3',4'-dichlorophenyl)3,3-dichloro-4-chloromethyl-2-pyrrolidinone
  - 9. 1-m-trifluoromethyl-3,3-dichloro-4-chloromethyl-2-pyrrolidinone
  - 10. N-m-trifluoromethylphenyl-3-chloro-3-methyl-3-chloromethyl-2-pyrrolidinone
  - 11. 1-p-tolyl-3-chloro-4-chloromethyl-2-pyrrolidinone

- 12. 1-m-fluorophenyl-3-chloro-4-chloromethyl-2-pyr-rolidinone
- 13. N-m-trifluoromethyl-3-bromo-4-bromomethyl-2-pyrrolidinone
- 14. N-3',4'-dichlorophenyl-3-chloro-4-chloromethyl-2- 5 pyrrolidinone
- 15. N-m-nitrophenyl-3-chloro-4-chloromethyl-2-pyr-rolidinone
- 16. N-3',5'-dichlorophenyl-3-chloro-4-chloromethyl-2-pyrrolidinone
- 17. N-m-trifluoromethylphenyl-3-chloro-4-(1-chloroe-thyl)-2-pyrrolidinone
- 18. N-m-cyanophenyl-3-chloro-4-chloromethyl-2-pyr-rollidinone
- 19. N-3,5-dichlorophenyl-3,3-dichloro-4-chloromethyl- <sup>15</sup> 2-pyrrolidinone
- 20. N-m-trifluoromethylphenyl-3,3-dichloro-4(1-chloroethyl)-2-pyrrolidinone
- 21. N-m-cyanophenyl-3,3-dichloro-4-chloromethyl-2-pyrrolidinone
- 22. N-3'-trifluoromethyl-4'-chlorophenyl-3-chloro-4-chloromethyl-2-pyrrolidinone
- 23. N-3'-trifluoromethyl-4'-chlorophenyl-3,3-dichloro-4-chloromethyl-2-pyrrolidinone
- 24. N-(m-trifluoromethylthiophenyl)-3-chloro-4-chloromethyl-2-pyrrolidinone
- 25. N(m-methylthiophenyl)-3-chloro-4-chloromethyl-2-pyrrolidinone
- 26. N(m-trifluoromethyl sulfinylphenyl)-3-chloro-4- 30 chloromethyl-2-pyrrolidinone
- 27. N-(m-methylsulfinylphenyl)-3-chloro-4-chloromethyl-2-pyrrolidinone
- 28. N(m-methylsulfonylphenyl)-3-chloro-4-chloromethyl-2-pyrrolidinone
- 29. N(m-trifluoromethylsulfonylphenyl)-3-chloro-4-chloromethyl-2-pyrrolidinone
- 30. N(3',5'-bis-trifluoromethylphenyl)-3-chloro-4-chloromethyl-2-pyrrolidone
- 31. N-m-methoxyphenyl-3-chloro-4-chloromethyl-2- 40 pyrrolidinone
- 32. N-m-acetylphenyl-3-chloro-4-chloromethyl-2-pyr-rolidinone
- 33. N-m-tolyl-3-chloro-4-chloromethyl-2-pyrrolidinone
- 34. N-m-trifluoromethylphenyl-4-chloromethyl-2-pyr- 45 rolidinone
- 35. N-m-bromophenyl-3-chloro-4-chloromethyl-2-pyr-rolidinone
- 36. N-o-chlorophenyl-N-3-chloro-4-chloromethyl-2-pyrrolidinone
- 37. N-m-iodophenyl-3-chloro-4-chloromethyl-2-pyr-rolidinone
- 38. N-p-methoxyphenyl-3-chloro-4-chloromethyl-2-pyrrolidinone
- 39. o-trifluoromethyl-3-chloro-4-chloromethyl-2-pyr- 55 rolidinone
- 40. N(m-pentafluoro propionamido phenyl) 3-chloro-4-chloromethyl-2-pyrrolidinone
- 41. N(m-methylureidophenyl) 3-chloro-4-chlorometh-yl-2-pyrrolidinone
- 42. cis 1-m-trifluoromethylphenyl-3-chloro-4-chloromethyl-2-pyrrolidinone
- 43. trans 1-m-trifluoromethylphenyl-3-chloro-4-chloromethyl-2-pyrrolidinone

## HERBICIDAL SCREENING TESTS

As previously mentioned, the herein described compounds produced in the above-described manner are

phytotoxic compounds which are useful and valuable in controlling various plant species. Compounds of this invention are tested as herbicides in the following manner.

### Pre-emergence Herbicide Screening Test

Using an analytical balance, 20 mg. of the compound to be tested is weighed out on a piece of glassine weighing paper. The paper and compound are placed in a 30 ml. wide-mouth bottle and 3 ml. of acetone containing 1% Tween 20 (R) (polyoxyethylene sorbitan monolaurate) is added to dissolve the compound. If the material is not soluble in acetone, another solvent such as water, alcohol or dimethylformamide (DMF) is used instead. When DMF is used, only 0.5 ml. or less is used to dissolve the compound and then another solvent is used to make the volume up to 3 ml. The 3 ml. of solution is sprayed uniformly on the soil contained in a small flat one day after planting weed seeds in the flat of soil. An atomizer is used to apply the spray using compressed air at a pressure of 5 lb./sq. inch. The rate of application is 8 lbs./acre and the spray volume is 143 gallons per acre.

On the day preceding treatment, the flat which is 7 inches long, 5 inches wide and 2.75 inches deep, is filled to a depth of 2 inches with loamy sand soil. Seeds of seven different weed species are planted in individual rows using one species per row across the width of the flat. The seeds are covered with soil so that they are planted at a depth of 0.5 inch. Ample seeds are planted to give about 20 to 50 seedlings per row after emergence depending on the size of the plants.

The seeds used are foxtail (Setaria spp.) — FT; watergrass (Echinochloa crusgalli) — WG; red oat (Avena sativa) — RO; redroot pigweed (Amaranthus retroflexus) — PW; mustard (Brassica juncea) — MD; curly dock (Rumex crispus) — CD; and hairy crabgrass (Digitaria sanguinalis) — CG.

After treatment, the flats are placed in the greenhouse at a temperature of 70° to 85° F. and watered by sprinkling. Two weeks after treatment, the degree of injury or control is determined by comparison with untreated check plants of the same age. The injury rating from 0 to 100% is recorded for each species as per cent control with 0% representing no injury and 100% representing complete kill.

## Post-emergence Herbicide Screening Test

Seeds of six plant species, including hairy crabgrass (CG), watergrass (WG), red oat (RO), mustard (MD), curly dock (CD) and Pinto beans (Phaseolus vulgaris) (BN), are planted in the flats as described above for pre-emergence screening. The flats are planted in the greenhouse at 70° to 85° F. and watered daily with a sprinkler. About 10 to 14 days after planting when the primary leaves of the bean plants are almost fully expanded and the first trifoliate leaves are just starting to 60 form, the plants are sprayed. The spray is prepared by weighing out 20 mg. of the test compound, dissolving it in 5 ml. of acetone containing 1% Tween 20® (polyoxyethylene sorbitan monolaurate) and then adding 5 ml. of water. The solution is sprayed on the foliage 65 using an atomizer at an air pressure of 5 lb./sq. inch. The spray concentration is 0.2% and the rate is 8 lb./acre. The spray volume is 476 gallons per acre.

The results of these tests are shown in Table II.

TABLE II

<u></u>		, <del>-</del> , -	Ŧ	IERBIC		– .	- SCRE trol at 8		RESULT	S			, <u> </u>		
COMPOUND		Pre-emergence							Post-emergence						
NUMBER	CG	FT	WG	RO	MD	CD	PW	CG	WG	RO	MD	CD	BN		
1	90	80	20	10	100	50	80	100	10	10	80	80	40		
2	100	100	40	0	100	50	80	100	0	0	80	20	. 0		
3	80	80	80	20	20	10	30	70	60	0	0	0	0		
4	100	100	100	50	100	100	100	100	95	50	100	100	100		
5***	70	30	0	0	0	0	0	95	0	0	90	40	0		
6	100	100	100	100	100	100	100	100	100	80	100	100	95		
7	90	10	10	0	10	0	0	80	20	0	90	80	60		
8	0	0	0	0	0	0	0	0	0	0	80	0	0		
9	100	100	100	30	100	100	98	90	80	10	100	100	100		
10	100	100	100	0	100	100	100	<del>9</del> 9	99	10	100	98	100		
11**	90	70	0	0	0	0	0	60	0	0	30	50	0		
12	100	100	100	<b>7</b> 0	100	100	100	100	100	50	100	100	- 95		
13	90	95	80	10	90	40	90	80	80	20	50	40	100		
14	30	30	0	0	40	40	0	30	20	0	50	0	10		
15	70	98	10	0	30	0	90	70	60	20	100	20	0		
16	90	90	10	0	30	30	90	95	50	10	100	80	80		
17	100	98	60	Ó	20	0	10	100	50	10	100	70	80		
18	100	100	100	98	100	100	98	100	100	100	100	100	80		
19	10	20	50	10	20	Õ	Õ	60	10	10	50	10	0		
20	95	10	60	Ō	10	Ŏ	10	90	20	0	95	50	10		
21	98	98	80	10	80	80	98	100	100	Ŏ	100	95	100		
22	100	100	80	30	95	40	95	100	70	90	100	100	100		
23	100	95	40	Õ	80	30	70	98	60	Ő	70	80	70		
24	100	100	100	9Š	98	98	95	100	90	9Š	100	80	100		
25	100	100	98	10	<b>80</b>	40	70	100	70	10	100	95	80		
26	100	100	100	30	98	98	95	100	70	60	100	100	100		
27	100	95	70	10	80	70	10	100	70 70	10	100	90	70		
28	100	100	98	10	95	50	10	100	70 70	20	100	95	80		
29	100	100	70	10	90	60	95	95	50	10	80	80	100		
30	100	100	80	10	80	60	60	100	80	40	80	80	10		
31	100	100	80	10	50	30	95	100	100	10	100	100	100		
32*	90	90	0	Ŏ	95	40	100	0	100	0	90	10	100		
33	100	100	80	ŏ	60	0	0	100	100	ő	100	95	ň		
34	100	100	98	Ö	90	95	98	100	100	10	100	100	100		
35	100	100	100	40	100	100	100	100	100	30	100	100	100		
36 <b>*</b>	100	100	98	0	98	98	100	100	80	10	100	80	40		
37	100	100	95	10	99	100	100	100		70		100			
38 <b>*</b>	30	20	۸ دو	10	_	100			98	/U	100	700	100		
39*	υ 30		U N	0	0	O O	0	0	. 0	V	20	Ŏ	U A		
	100	0	10	V	100	0 50	0	10	Ď.	Ŭ	30	100	Ü		
40 41	100	95 90	10	Ú	100	50 05	98 70	95 100	<b>U</b>	Ŭ	100	100	100		
41	100	90	70	U	95	95	70	100	20	Ū	100	100	100		

<sup>\*=</sup>SCREENING RESULTS - Per cent control at 20 lb/A pre- and post-emergence

Compounds 42 (cis) and 43 (trans) were bioassayed in the herbicide screen employing the pre-emergence surface technique. The following results in Table III were 40 obtained at 0.25 lb/A, 0.5 lb/A and 1.0 lb/A. A mixture of approximately 40% cis and 60% trans is included for comparison and to show the preferred activity of the cis-configuration.

wetting, dispersing or emulsifying agents. An herbicidally effective amount depends upon the nature of the seeds or plants to be controlled and the rate of application varies from 0.10 to approximately 50 pounds per acre. The concentration of a compound of the present invention, constituting an effective amount in the best mode of administration in the utility disclosed, is readily

TABLE III

COMPOUND/	Rate						<u> </u>		Avg.	
CONFIGURATION	(lb/A)	CG	FT	WG	wo	PB	AMG	COT	GR	BL
42 - cis	0.25	100	100	80	10	20	40	20	73	27
	0.5	100	100	99	60	50	30	20	90	33
•	1.0	100	100	100	80	80	70	50	95	67
43 - trans	0.25	97	10	20	0	0	0	0	32	0
	0.5	98	70	40	0	0	0	0	52	0
	1.0	100	100	80	10	20	0	0	73	7
Mixture	0.25	100	100	60	0	10	0	Ö	65	3
(40:60)	0.5	100	100	90	30	40	20	10	80	23
	1.0	100	100	100	60	60	50	20	90	43

CG, FT, WG and WO = crabgrass, foxtail, watergrass and wild oats

PB, AMG and COT = pinto bean, annual morning glory (Ipomoea purpurea), and cotton (Ipomoea trichocarpa)

The compounds of the present invention are used as preemergence or post-emergence herbicides and are applied in a variety of ways of various concentrations. 60 In practice, the compounds are formulated with an inert carrier, utilizing methods well known to those skilled in the art, thereby making them suitable for application as dusts, sprays, or drenches and the like, in the form and manner required. The mixtures can be dispersed in 65 water with the aid of a wetting agent or they can be employed in organic liquid compositions, oil and water, water in oil emulsions, with or without the addition of

determinable by those skilled in the art.

The phytotoxic compositions of this invention employing an herbicidally effective amount of the compound described herein are applied to the plants in the conventional manner. The present invention contemplates methods of selectively killing, combatting or controlling undesired plants which comprises applying to at least one of (a) such weeds and (b) their habitat, that is, the locus to be protected, an herbicidally effective or toxic amount of the particular active compound

<sup>\*\*=</sup> Pre-emergence Screening Results at 20 lb/A

\*\*\*= Post-emergence Screening Results at 20 lb/A

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alone or together with a carrier or adjuvant. Thus, the dust and liquid compositions can be applied to the plant by the use of power dusters, boom and hand sprayers and spray dusters. The compositions can also e applied from airplanes as a dust or a spray because they are effective in very low dosages. In order to modify or control growth of germinating seeds or emerging seedlings, as a typical example, the dust and liquid compositions are applied to the soil according to conventional methods and are distributed in the soil to a depth of at 10 least one-half inch below the soil surface. It is not necessary that the phytotoxic compositions be admixed with the soil particles and these compositions can be applied merely by spraying or sprinkling the surface of the soil. The phytotoxic compositions of this invention can also 15 be applied by addition to irrigation water supplied to the field to be treated. This method of application permits the penetration of the compositions into the soil as the water is absorbed therein. Dust compositions, granular compositions or liquid formulations applied to the 20 surface of the soil can be distributed below the surface of the soil by conventional means such as discing, dragging or mixing operations.

The phytotoxic compositions of this invention can also contain other additaments, for example, fertilizers, 25 pesticides and the like, used as adjuvant or in combination with any of the above-described adjuvants. Other phytotoxic compounds useful in combination with the above-described compounds include, for example, 2,4dichlorophenoxyacetic acids, 2,4,5-trichlorophenoxya-30 cetic acid, 2-methyl-4-chlorophenoxyacetic acid and the salts, esters and amides thereof; triazine derivatives, such as 2,4-bis(3-methoxypropylamino)-6-methyl-thios-triazine; 2-chloro-4-ethylamino-6-isopropylamino-striazine, and 2-ethylamino-4-isopropylamino-6-methyl- 35 mercapto-s-triazine, urea derivatives, such as 3-(3,4dichlorophenyl)-1,1-dimethyl urea and acetamides such as N,N-diallyl- $\alpha$ -chloroacetamide, N-( $\alpha$ -chloroacetyl)hexamethyleneimine, and N,N-diethyl-α-bromoacetamide, and the like; benzoic acids such as 3-amino-2,5dichlorobenzoic; and thiocarbamates, such as S-propyl dipropylthiocarbamate; S-ethyldipropylthiocarbamate; S-ethyl hexahydro-1H-azepine-1-carbothioate and the like. Fertilizers useful in combination with the active ingredients include, for example, ammonium nitrate, 45 urea and superphosphate. Other useful additaments include materials in which plant organisms take root and grow, such as compost, manure, humus, sand and the like.

Various changes and modifications are possible without departing from the spirit and scope of the invention described herein and will be apparent to those skilled in the art to which it pertains. It is accordingly intended that the present invention shall only be limited by the scope of the claims.

What is claimed is:

1. A compound having the formula

$$Z-CH-C-CH_{2}$$

$$R_{2}$$

$$R_{2}$$

$$R$$

$$R_{3}$$

in which X is hydrogen, chlorine or methyl; Y is hydrogen, chlorine or bromine, Z is chlorine or bromine; R<sub>2</sub> is alkyl having from 1 to 4 carbon atoms, inclusive, or

hydrogen; R is hydrogen, alkyl, acetyl, chlorine, bromine, fluorine, iodine, trifluoromethyl, nitro, cyano, alkoxy having from 1 to 4 carbon atoms, inclusive, alkylsulfinyl having from 1 to 4 carbon atoms, inclusive, alkylsulfinyl having from 1 to 4 carbon atoms, inclusive, alkylsulfonyl having from 1 to 4 carbon atoms, inclusive, trifluoromethylthio, trifluoromethylsulfinyl, trifluoromethylsulfonyl, penta fluoropropionamido or 3-methylureido; and R<sub>1</sub> is hydrogen, alkyl having from 1 to 4 carbon atoms, inclusive, chlorine or trifluoromethyl.

2. The compound according to claim 1 in which X is hydrogen, Y is chlorine, Z is chlorine, R,  $R_1$  and  $R_2$  are each hydrogen.

3. The compound according to claim 1 in which X is chlorine, Y is chlorine, Z is chlorine, R,  $R_1$  and  $R_2$  are each hydrogen.

4. The compound according to claim 1 in which X is methyl, Y is chlorine, Z is chlorine, R,  $R_1$  and  $R_2$  are each hydrogen.

5. The compound according to claim 1 in which X is hydrogen, Y is chlorine, Z is chlorine,  $R_2$  is hydrogen, R is methyl, acetyl, chlorine, bromine, fluorine, iodine, trifluoromethyl, nitro, cyano, trifluoromethylthio, trifluoromethylsulfinyl, trifluoromethylsulfonyl, alkylthio, alkylsulfinyl, alkylsulfonyl, pentafluoropropionamido, or 3-methylureido, and  $R_1$  is hydrogen.

6. The compound according to claim 5 in which R is 4-methyl.

7. The compound according to claim 5 in which R is 3-fluorine.

8. The compound according to claim 5 in which R is 3-chlorine.

9. The compound according to claim 5 in which R is 4-chlorine.

10. The compound according to claim 5 in which R is 3-trifluoromethyl.

11. The compound according to claim 5 in which R is 3-nitro.

12. The compound according to claim 5 in which R is 3-cyano.

13. The compound according to claim 5 in which R is 3-trifluorothio.

14. The compound according to claim 5 in which R is 3-trifluorosulfinyl.

15. The compound according to claim 5 in which R is 3-trifluorosulfonyl.

16. The compound according to claim 5 in which R is 3-methylthio.

17. The compound according to claim 5 in which R is 3-methylsulfinyl.

18. The compound according to claim 5 in which R is 3-methylsulfonyl.

19. The compound according to claim 5 in which R is 3-methoxy.

20. The compound according to claim 5 in which R is 3-acetyl.

21. The compound according to claim 5 in which R is 3-methyl.

22. The compound according to claim 5 in which R is 3-bromine.

23. The compound according to claim 5 in which R is 2-chlorine.

24. The compound according to claim 5 in which R is 3-iodine.

25. The compound according to claim 5 in which R is 4-methoxy.

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26. The compound according to claim 5 in which R is 2-trifluoromethyl.

27. The compound according to claim 5 in which R is 3-pentafluoropropionamido.

28. The compound according to claim 5 in which R is 5 3-(3-methylureido).

29. The compound according to claim 5 in which said compound is the cis-isomer configuration.

30. The compound according to claim 29 in which R is 3-trifluoromethyl.

31. The compound according to claim 5 in which said compound is the trans-isomer configuration.

32. The compound according to claim 31 in which R is 3-trifluoromethyl.

33. The compound according to claim 1 in which X is 15 hydrogen, Y is chlorine, Z is chlorine,  $R_2$  is hydrogen, R is alkyl and  $R_1$  is alkyl.

34. The compound according to claim 33 in which R is 2-methyl and  $R_1$  is 6-methyl.

35. The compound according to claim 1 in which X is 20 chlorine, Y is chlorine, Z is chlorine,  $R_2$  is hydrogen, R is chlorine, trifluoromethyl or cyano, and  $R_1$  is hydrogen or chlorine.

36. The compound according to claim 35 in which R is 3-chlorine, and R<sub>1</sub> is 4-chlorine.

37. The compound according to claim 35 in which R is 3-trifluoromethyl and  $R_1$  is hydrogen.

38. The compound according to claim 35 in which R is 3-chlorine and  $R_1$  is 5-chlorine.

39. The compound according to claim 35 in which R 30 is 3-cyano and R<sub>1</sub> is hydrogen.

40. The compound according to claim 35 in which R

40. The compound according to claim 35 in which R is 3-trifluoromethyl and  $R_1$  is 4-chlorine.

41. The compound according to claim 1 in which X is hydrogen, Y is bromine, Z is bromine,  $R_2$  is hydrogen, R 35 is 3-trifluoromethyl and  $R_1$  is hydrogen.

42. The compound according to claim 1 in which X is methyl, Y is chlorine, Z is chlorine,  $R_2$  is hydrogen, R is 3-trifluoromethyl and  $R_1$  is hydrogen.

43. The compound according to claim 1 in which X is 40 hydrogen, Y is chlorine, Z is chlorine, R<sub>2</sub> is hydrogen, R is 3-chlorine and R<sub>1</sub> is 5-chlorine.

44. The compound according to claim 1 in which X is hydrogen, Y is chlorine, Z is chlorine,  $R_2$  is methyl, R is 3-trifluoromethyl and  $R_1$  is hydrogen.

45. The compound according to claim 1 in which X is chlorine, Y is chlorine, Z is chlorine,  $R_2$  is methyl, R is 3-trifluoromethyl and  $R_1$  is hydrogen.

46. The compound according to claim 1 in which X is hydrogen, Y is chlorine, Z is chlorine, R is 3-chlorine 50 and R<sub>1</sub> is 4-chlorine.

47. The compound according to claim 1 in which X is hydrogen, Y is chlorine, Z is chlorine, R is 3-tri-fluoromethyl and  $R_1$  is 4-chlorine.

48. The compound according to claim 1 in which X is 55 hydrogen, Y is chlorine, Z is chlorine, R is 3-tri-fluoromethyl and  $R_1$  is 5-trifluoromethyl.

49. The compound according to claim 1 in which X is hydrogen, Y is hydrogen, Z is chlorine, R is methyl, acetyl, chlorine, bromine, fluorine, iodine, trifluoro- 60 methyl, nitro, cyano, trifluoromethylthio, trifluoromethylsulfinyl, trifluoromethylsulfonyl, alkylthio, alkylsulfinyl, alkylsulfonyl, pentafluoropropionamido, or 3-methylureido, and R<sub>1</sub> and R<sub>2</sub> are each hydrogen.

50. The compound according to claim 49 in which R 65 is 3-trifluoromethyl.

51. A method for controlling the growth of undesirable vegetation which comprises applying to at least

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one of (a) such undesirable vegetation and (b) their habitat, an herbicidally effective amount of a compound having the formula

in which X is hydrogen, chlorine or methyl; Y is hydrogen, chlorine or bromine, Z is chlorine or bromine; R<sub>2</sub> is alkyl having from 1 to 4 carbon atoms, inclusive, or hydrogen; R is hydrogen, alkyl, acetyl, chlorine, bromine, fluorine, iodine, trifluoromethyl, nitro, cyano, alkoxy having from 1 to 4 carbon atoms, inclusive, alkylsulfinyl having from 1 to 4 carbon atoms, inclusive, alkylsulfinyl having from 1 to 4 carbon atoms, inclusive, alkylsulfonyl having from 1 to 4 carbon atoms, inclusive, trifluoromethylthio, trifluoromethylsulfinyl, trifluoromethylsulfonyl, pentafluoroproprionamido, or 3-methylureido; and R<sub>1</sub> is hydrogen, alkyl having from 1 to 4 carbon atoms, inclusive, chlorine or trifluoromethyl.

52. The method according to claim 51 in which X is hydrogen, Y is chlorine, Z is chlorine, R, R<sub>1</sub> and R<sub>2</sub> are each hydrogen.

53. The method according to claim 51 in which X is chlorine, Y is chlorine, Z is chlorine, R,  $R_1$  and  $R_2$  are each hydrogen.

54. The method according to claim 51 in which X is methyl, Y is chlorine, Z is chlorine, R,  $R_1$  and  $R_2$  are each hydrogen.

55. The method according to claim 51 in which X is hydrogen, Y is chlorine, Z is chlorine, R<sub>2</sub> is hydrogen, R is methyl, acetyl, chlorine, bromine, fluorine, iodine, trifluoromethyl, nitro, cyano, trifluoromethylthio, trifluoromethylsulfinyl, trifluoromethylsulfonyl, alkylthio, alkylsulfinyl, alkylsulfonyl, pentafluoropropionamido, or 3-methylureido; and R<sub>1</sub> is hydrogen.

56. The method according to claim 55 in which R is 4-methyl.

57. The method according to claim 55 in which R is 3-fluorine.

58. The method according to claim 55 in which R is 3-chlorine.

59. The method according to claim 55 in which R is 4-chlorine.

60. The method according to claim 55 in which R is 3-trifluoromethyl.

61. The method according to claim 55 in which R is 3-nitro.

62. The method according to claim 55 in which R is 3-cyano.

63. The method according to claim 55 in which R is 3-trifluorothio.

64. The method according to claim 55 in which R is 3-trifluorosulfinyl.

65. The method according to claim 55 in which R is 3-trifluorosulfonyl.

66. The method according to claim 55 in which R is 3-methylthio.

67. The method according to claim 55 in which R is 3-methylsulfinyl.

68. The method according to claim 55 in which R is 3-methylsulfonyl.

- 69. The method according to claim 55 in which R is 3-methoxy.
- 70. The method according to claim 55 in which R is 3-acetyl.
- 71. The method according to claim 55 in which R is 3-methyl.
- 72. The method according to claim 55 in which R is 3-bromine.
- 73. The method according to claim 55 in which R is 2-chlorine.
- 74. The method according to claim 55 in which R is 3-iodine.
- 75. The method according to claim 55 in which R is 4-methoxy.
- 76. The method according to claim 55 in which R is 2-trifluoromethyl.
- 77. The method according to claim 55 in which R is 3-pentafluoropropionamido.
- 78. The method according to claim 55 in which R is 3-(3-methylureido).
- 79. The method according to claim 55 in which said compound is the cis-isomer configuration.
- 80. The method according to claim 79 in which R is 3-trifluoromethyl.
- 81. The method according to claim 55 in which said compound is the trans-isomer configuration.
- 82. The method according to claim 81 in which R is 3-trifluoromethyl.
- 83. The method according to claim 51 in which X is hydrogen, Y is chlorine, Z is chlorine,  $R_2$  is hydrogen, R is alkyl and  $R_1$  is alkyl.
- 84. The method according to claim 83 in which R is 2-methyl and  $R_1$  is 6-methyl.
- 85. The method according to claim 51 in which X is chlorine, Y is chlorine, Z is chlorine, R<sub>2</sub> is hydrogen, R

- is chlorine, trifluoromethyl or cyano, and  $R_1$  is hydrogen or chlorine.
- 86. The method according to claim 85 in which R is 3-chlorine, and R<sub>1</sub> is 4-chlorine.
- 87. The method according to claim 85 in which R is 3-trifluoromethyl and  $R_1$  is hydrogen.
- 88. The method according to claim 85 in which R is 3-chlorine and  $R_1$  is 5-chlorine.
- 89. The method according to claim 85 in which R is 3-cyano and R<sub>1</sub> is hydrogen.
  - 90. The method according to claim 85 in which R is 3-trifluoromethyl and R<sub>1</sub> is 4-chlorine.
- 91. The method according to claim 51 in which X is hydrogen, Y is bromine, Z is bromine, R<sub>2</sub> is hydrogen, R is 3-trifluoromethyl and R<sub>1</sub> is hydrogen.
  - 92. The method according to claim 51 in which X is methyl, Y is chlorine, Z is chlorine,  $R_2$  is hydrogen, R is 3-trifluoromethyl and  $R_1$  is hydrogen.
  - 93. The method according to claim 51 in which X is hydrogen, Y is chlorine, Z is chlorine,  $R_2$  is hydrogen, R is 3-chlorine and  $R_1$  is 5-chlorine.
  - 94. The method according to claim 51 in which X is hydrogen, Y is chlorine, Z is chlorine,  $R_2$  is methyl, R is 3-trifluoromethyl and  $R_1$  is hydrogen.
  - 95. The method according to claim 51 in which X is chlorine, Y is chlorine, Z is chlorine,  $R_2$  is methyl, R is 3-trifluoromethyl and  $R_1$  is hydrogen.
- 96. The method according to claim 51 in which X is hydrogen, Y is chlorine, Z is chlorine, R<sub>2</sub> is hydrogen, R is 3-chlorine and R<sub>1</sub> is 4-chlorine.
  - 97. The method according to claim 51 in which X is hydrogen, Y is chlorine, Z is chlorine,  $R_2$  is hydrogen, R is 3-trifluoromethyl and  $R_1$  is 4-chlorine.
- 98. The method according to claim 51 in which X is hydrogen, Y is chlorine, Z is chlorine, R<sub>2</sub> is hydrogen, R is 3-trifluoromethyl and R<sub>1</sub> is 5-trifluoromethyl.

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